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Porous Organic Polymers Based on Propeller-Like Hexaphenylbenzene Building Units

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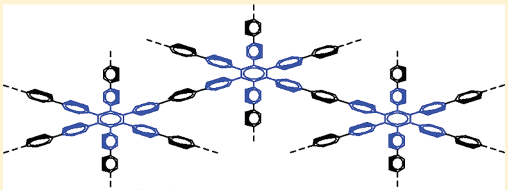
S *Supporting Information*

ABSTRACT: Hexaphenylbenzene-based porous organic polymers are prepared smoothly through palladium-catalyzed C−C coupling polymerization. According to the obtained nitrogen physisorption isotherms, the Brunauer−Emmett−Teller specific surface area for these polymers varies between 742 and 1148 m^2 g^{-1}. Gravimetric hydrogen adsorption isotherms show that the adsorption capacity for hydrogen is up to 1.5 wt % at 1.13 bar and 77 K. Thanks to the propeller-like structure, unique electronic feature, and efficient preparation, hexaphenylbenzene can be taken as a promising building block for designing porous polymers with special properties.

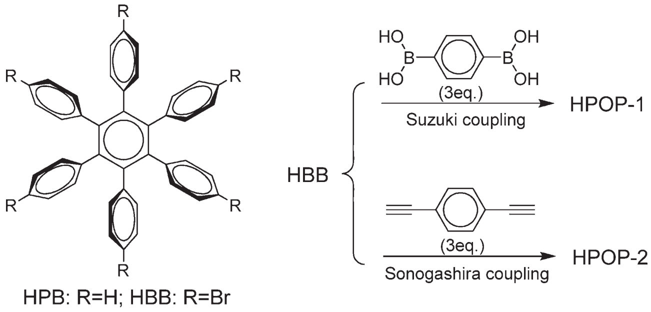


S_{BET}: 1148 m^2 g^{-1}, H_2 uptake: 1.5 wt% (77 K, 1.13 bar)

Because of the intrinsic properties of large specific surface area, high chemical stability, and low skeleton density,[1] porous organic polymers (POPs) have drawn great interests of scientists in recent years. In general, POPs are categorized into several classes, such as hyper-cross-linked polymers (HCPs),[2] polymers of intrinsic microporosity (PIMs),[3] covalent organic frameworks (COFs),[4] and conjugated microporous polymers (CMPs),[5] which exhibit potential applications in heterogeneous catalysis[6] and gas storage.[7] Building units play crucial roles in exploring the porosity, porous structure, and gas adsorption capacities of the POPs. Versatile POPs can be obtained by selection of proper building blocks, which show high flexibility in the molecular design. For example, spiro-cyclic compounds, as the rigid, contorted building blocks, have been employed in preparation of solution-processable PIMs[8] and CMPs[9] with large specific surface area. The planar π−system molecules, such as triphenylene and pyrene, are the monomers used in construction of the luminescent and semiconducting COFs.[10] The tetrahedral carbon- and silicon-centered building units can also be employed in synthesis of organic materials with an exceptional hydrogen storage.[11] Recently, the cubic siloxane-cages[12] and bulky adamantane[13] have been used in preparing porous polymers.

Owing to the steric effect of the peripheral phenyl rings, hexaphenylbenzene (HPB) exhibits a propeller-like nonplanar conformation (Scheme 1),[14] which is different from the structures of those aforementioned organic molecules. The propeller-like conformation enables π−π interaction between the peripheral aromatic rings facing each other, and the resulting sextuple accumulation of the π−π interaction would lead to the so-called "toroidal delocalization".[14,15] Therefore, HPB has been regarded as one of the promising three-dimensional topologies and is expected to exhibit unique electronic features.[16] Thanks to its efficient preparation and propeller-like structure, HPB is expected to be a novel building unit for design of porous organic polymers, and use of HPBs as components for making polymers of intrinsic microporosity, HPB-PIM, has been reported very recently (after our submission).[17] Herein, preparation and sorption properties of HPB-based porous organic polymers (HPOPs) via palladium-catalyzed C−C coupling polycondensation are reported. Compared with HPB-PIM, the HPOPs exhibit a much higher BET specific surface area and can be obtained more efficiently. The Brunauer−Emmett−Teller (BET) specific surface area for these polymers ranges from 742 to 1148 m^2 g^{-1}.

Scheme 1. Preparation of HPOPs by Palladium-Catalyzed C−C Coupling Polycondensation



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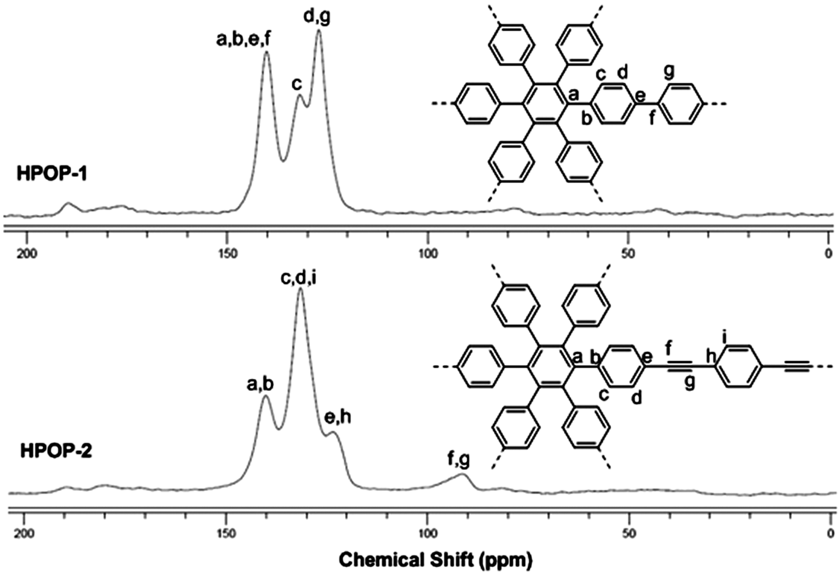

Figure 1. ^{13}C CP/MAS NMR spectra of the HPOPs.

Gravimetric hydrogen adsorption isotherms show that the hydrogen uptake of the synthetic POPs is up to 1.5 wt % at 1.13 bar and 77 K.

Hexakis(4-bromophenyl)benzene (HBB), as the derivative of HPB, also shows the similar conformation and can be easily obtained up to kilogram scale with low-cost,[18] which is a perfect monomer for construction of POPs with potential applications. As shown in Scheme 1, HPOP-1 and HPOP-2 can be prepared in high yields from HBB through Suzuki coupling polymerization and Sonogashira–Hagihara coupling polymerization, which are reliable methods to furnish POPs proved by Thomas group[19] and Cooper group,[5a] respectively. All of the polymers are chemically stable, even exposed to dilute solution of acid or base, such as chloric acid or sodium hydroxide. Thermal analysis (Supporting Information, Figure S1) shows that the materials are stable up to 400 °C in all cases under nitrogen and has no evidence for distinct glass transition for these polymers below the thermal decomposition temperature due to the nature of their cross-linking structures, which are consistent with the good physico-chemical robustness for most porous organic polymers.[20] In order to confirm their structures, two polymers were characterized at the molecular level by ^{13}C CP/MAS NMR. The ^{13}C NMR spectra for the porous polymers with assignment of the resonances are shown in Figure 1. For HPOP-1, there are three broad peaks at approximately 140.0, 131.7, and 127.1 ppm, respectively. The peak at 140.0 ppm corresponds to the substituted phenyl carbons, and the peaks at 131.7 and 127.1 ppm show the unsubstituted phenyl carbons. As to HPOP-2, the peak at 140.0 ppm corresponds to nonacetylene-substituted phenyl carbons. The peaks at 131.4 and 123.3 ppm show the unsubstituted phenyl carbons and acetylene-substituted phenyl carbons. Furthermore, the low-intensity peak at approximately 91.1 ppm can be ascribed to acetylene carbons. The ^{13}C CP/MAS NMR spectrum for the triple-bond linkage of the HPOP-2 is also consistent with the data obtained by FT-IR measurement, in which the triple bond of acetylene carbon yields the signal at 2200 cm^{-1}. (Supporting Information, Figure S2)

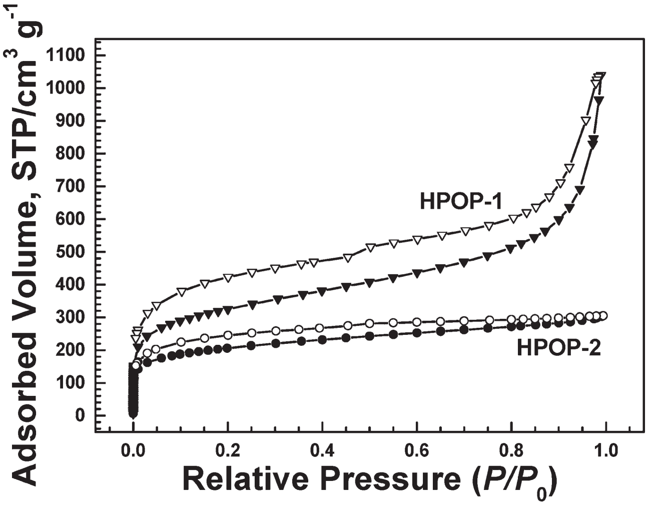

Figure 2. Nitrogen adsorption–desorption isotherms measured at 77 K (the adsorption and desorption branches are labeled with solid and open symbols, respectively).

The porosity parameters of the polymers were studied by sorption analysis using nitrogen as the sorbate molecule. Nitrogen adsorption–desorption isotherms of two HPOPs measured at 77 K are shown in Figure 2. HPOP-2 possesses a type I nitrogen gas sorption isotherm according to the IUPAC classification[21] and shows a very flat sorption plateau, indicating that the material is microporous. The nitrogen isotherm for HPOP-1 differs substantially at the higher relative pressure range and exhibits a combination of type I and II nitrogen sorption isotherms. The isotherms show a continuous increase after the adsorption at low relative pressure, indicating an adsorption on the outer surface of small particles. The increase in the nitrogen sorption at a high relative pressure above 0.9 may arise in part from interparticulate porosity associated with the meso- and macrostructures of the samples and interparticular void.[5a,22] In addition, a hysteresis can be observed for the whole range of relative pressure based on the isotherms due to a linear increase of the adsorbed volume upon adsorption, which is attributed to the swelling in a flexible

Table 1. Porosity and Hydrogen Uptake Capacities of HPOPs

polymers	S_{BET} ($m^2\ g^{-1}$)[a]	S_{micro} ($m^2\ g^{-1}$)[b]	V_{total} ($cm^3\ g^{-1}$)[c]	V_{micro} ($cm^3\ g^{-1}$)[d]	hydrogen uptake (wt %)[e]
HPOP-1	1148 (1277)	352	1.283	0.154	1.50
HPOP-2	742 (825)	328	0.457	0.137	1.08

[a] Specific surface area calculated from the nitrogen adsorption isotherm using the BET method. The number in parentheses is the Langmuir specific surface area calculated from the nitrogen adsorption isotherm by application of the Langmuir equation. [b] The specific surface area for the micropores calculated from the nitrogen adsorption isotherm using the *t*-plot method. [c] Total pore volume at $P/P_0 = 0.97$. [d] Micropore volume derived using the *t*-plot method based on the Halsey thickness equation. [e] Data are obtained at 1.13 bar and 77 K.

polymer framework induced by adsorbate molecules dissolved in nominally nonporous parts of the polymer matrix after filling of open and accessible voids[23] or the restricted access of adsorbate to the pores blocked by narrow openings, especially for non-ordered nanoporous materials.[22,24]

Listed in Table 1 are the key structural properties derived from the isotherm data such as BET and Langmuir specific surface area data, micropore specific surface area data, and micropore volumes. As for determination of the specific surface area, the relative pressure range (P/P_0) commonly used is 0.05−0.2. However, in some cases, it can not give a good fit for microporous materials.[25] Alternatively, a narrower pressure range at $P/P_0 < 0.1$ instead of 0.05−0.2 is used.[26] The BET specific surface area values for HPOPs calculated over these two different pressure ranges (Supporting Information, Figures S3 and S4) are found to be very close to each other (Supporting Information, Table S1), especially for HPOP-1 (1148 and 1147 $m^2\ g^{-1}$). The BET and Langmuir specific surface area data listed in Table 1 are determined from the relative pressure range of 0.01−0.1. The BET specific surface area values for the polymers HPOP-1 and HPOP-2 are 1148 and 742 $m^2\ g^{-1}$, respectively. As for HPOP-1, the BET specific surface area is not only comparable to most porous polymers obtained previously using similar coupling chemistry, but also higher than most of the reported PIM networks. It should be noted that HPOPs featuring different specific surface areas can be obtained, when the ratio of HBB to BDBA varies. The decrease in the amount of BDBA in the polymer preparation leads to a significant decrease in the resulting specific surface area. Compared with HPOP-1 (the monomer ratio is 1:3), the BET specific surface area of the porous polymer obtained by the monomer ratio of 1:2 decreases from 1148 to 760 $m^2\ g^{-1}$. Probably due to the lower cross-linking density, the pores in the latter polymer are less stable and easily collapse, leading to the decreased specific surface area. For the nonordered porous materials, accurate determination of the pore size distribution (PSD) is very difficult. Different results are usually obtained according to different approaches. PSD analysis based on the nonlocal density function theory (NLDFT) approach has been used extensively to characterize a wide variety of porous materials although it does have some limitations.[23] However, the calculated results can give some related qualitative information, with which one can make a relative comparison of materials synthesized from different monomers. As shown in Figure S5 (Supporting Information), the pore size distributions of HPOPs were calculated from the NLDFT approach. The HPOPs exhibit similar PSDs with dominant pore width at 0.63 nm. The overall micropore volume falls from HPOP-1 (1.28 $cm^3\ g^{-1}$) to HPOP-2 (0.46 $cm^3\ g^{-1}$) as the length of the monomer linker increases. This observation is consistent with the trends in specific surface area calculated using the BET model (nitrogen as the sorbate gas). HPOP-1 with the shorter linker possesses BET specific surface area (1148 $m^2\ g^{-1}$), which is higher than that of HPOP-2.

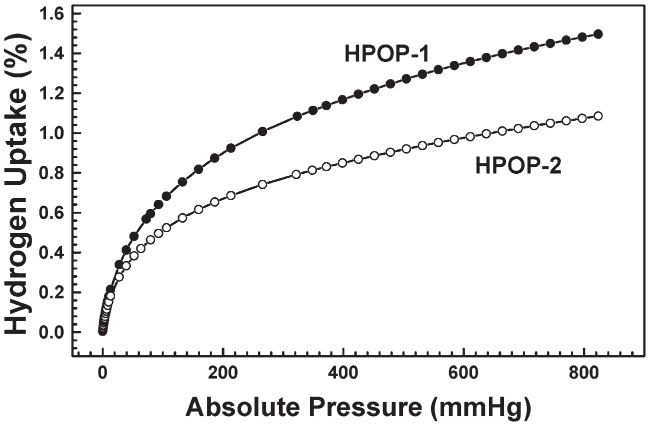

Figure 3. Gravimetric hydrogen adsorption isotherms at 77 K.

On account of the high capacity in hydrogen adsorption for many porous materials, we investigated their hydrogen uptake capacity based on the hydrogen physisorption isotherms measured at 77 K up to a pressure of 1.13 bar (Figure 3). An increase in the total hydrogen capacity with increasing specific surface area is observed. Among the series of HPOPs we investigated, HPOP-1, possessing the highest BET specific surface area and the highest micropore volume, exhibits the largest hydrogen uptake of 1.5 wt % at 1.13 bar and 77 K. The hydrogen uptake capacity of HPOP-1 is comparable to or higher than some previously obtained porous organic polymers with a higher specific surface area, such as imine-linked microporous polymer organic framework POF A1-B2 (1.5 wt % at 1 bar, 77 K, $S_{BET} = 1380\ m^2\ g^{-1}$),[27] porous polyporphyrin containing Fe−porphyrin complex P(Fe-TTPP) (~1.5 wt % at 1 bar, 77 K, $S_{BET} = 1248\ m^2\ g^{-1}$),[28] the conjugated microporous polymer based on spirobipropylenedioxythiophene SPT-CMP 2 (1.57 wt % at 1.13 bar, 77 K, $S_{BET} = 1601\ m^2\ g^{-1}$),[9a] the element organic framework EOF-6 (1.29 wt % at 1 bar, 77 K, $S_{BET} = 1380\ m^2\ g^{-1}$),[22] and SPT-CMP 3 (~1.34 wt % at 1.13 bar, 77 K, $S_{BET} = 1334\ m^2\ g^{-1}$).[9a]

As expected, all HPB-based nanoporous polymers show a nonordered, amorphous structure proved by the X-ray diffraction measurements, due to the kinetic control of the reaction. Figure 4 shows the scanning electron microscopy images and high-resolution transmission electron microscopy images of polymer HPOP-1, in which SEM analysis of HPOP-1 (Figure 4, parts a and b) displays that the polymer consists of relatively uniform solid submicrometer spheres. This kind of mesostructure was also found for homocoupled conjugated microporous polymer (HCMPs)[29] produced from 1,3,5-triethynylbenzene, which implies that HCMPs and HPOPs have a similar phase separation process. Small macropores or mesopores in the two polymers can be ascribed mostly to the interparticulate porosity existing between agglomerated microgel particles.[29] The TEM images (Figure 4, parts c and d) are indicative of porous structures of the materials, which is similar to some reported amorphous microporous organic materials.[5a]

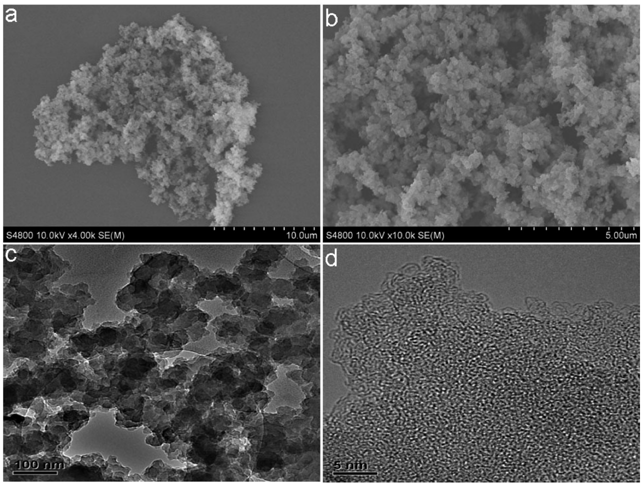

Figure 4. SEM images (a and b) and TEM images (c and d) of HPOP-1.

In conclusion, using hexaphenylbenzene as a core building unit, HPOPs have been successfully prepared through palladium-catalyzed C—C coupling condensation. The BET specific surface area for these polymers is up to 1148 m^2 g^{-1}. Gravimetric hydrogen adsorption isotherms show that the adsorption capacity for hydrogen is 1.5 wt % at 1.13 bar and 77 K. Because of the steric effect of the peripheral phenyl rings, HPB exhibits a propeller-like nonplanar conformation, which is different from the previously used core structure monomers for porous organic polymers, such as contorted spiro-cyclic compounds, planar π-system molecules, and tetrahedral carbon- and silicon-centered building blocks. Various POPs based on other propeller-like core structure monomers have been prepared and the related porosities and gas sorption analysis are under study.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Details of experimental materials and measurements, synthetic procedures of the HPOPs, TGA data of HPOPs, FT-IR spectrum of HPOP-2, BET specific surface areas of HPOPs calculated over different pressure ranges, pore size distribution of HPOP-1 and HPOP-2 calculated by NLDFT. This material is available free of charge via the Internet at http://pubs.acs.org.

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